IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Patent Application of

NEUMAN et al. Atty. Ref.: 3691-641; Confirmation No.

Appl. No. 10/777,191 TC/A.U. 1775

Filed: February 12, 2004 Examiner: Blackwell-Rudasill, G.

For: HEAT TREATABLE COATED ARTICLES WITH METAL NITRIDE LAYER AND METHODS OF MAKING SAME

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March 7, 2005

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

RULE 131 DECLARATION OF HONG WANG

I, Hong Wang, am an inventor of the instant application and hereby declare as follows:

1. I work for Guardian Industries Corp., assignee of the instant application.

2. I have been working in the art of glass coatings and materials for many years, and am an inventor listed on numerous United States Patents.

3. I am a co-inventor listed on the above-listed patent application (10/777,191), which I am familiar with. It is my understanding that certain example non-limiting embodiments of this invention relate to a layer stack of glass/Si_3N_4/$NiCrN_x$/Si_3N_4, although other materials may possibly be used instead.

4. Attached hereto as Exhibit A is a report entitled "Sun-Guard Silver Development Corsicana Experimentation Report Rune Date: 1/23 to 1/24/01." Exhibit A indicates that certain

example embodiments of this invention were reduced to practice at least as early as January of 2001. The examples listed in Exhibit A which were reduced to practice had the following layer stack: glass/Si_3N_4/$NiCrN_x$/Si_3N_4. These samples were heat treated and had a delta-E* value of no greater than 4.0 after heat treatment. Other samples having a stack of glass/Si_3N_4/$NiCrN_x$/Si_3N_4 were also made prior to March 29, 2001. Certain samples were tested and were chemically durable in that before and/or after heat treatment showed no visible discoloration and no visible peeling after a reference of about a one hour boil of a sample in 5% HCl solution at about 220 degrees F.

5. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Respectfully submitted,

By: _____ 3/07/05
Hong Wang

Sun-Guard Silver Development
Corsicana Experimentation Report
Run Date: 1/23 to 1/24/01

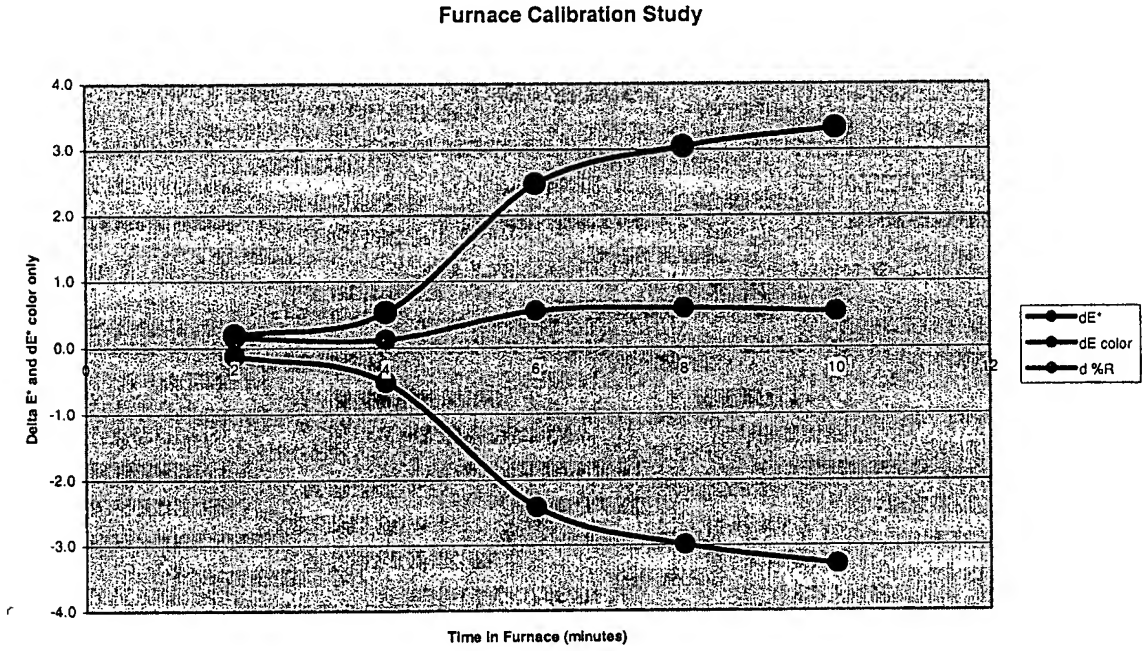
George Neuman & Leonard Holmes

Objective: To determine the effect of process parameters (and resultant coating changes) on color and sheet resistance changes with heat treatment.

Preliminary Experiments:

Experiments conducted by Corsicana before the run.

1. The color shift and sheet resistance shift with heat treating in the small furnace did not change much between 2 and 4 minutes but a jump occurred between 4 and 6 minutes and remained substantially constant. Our previous practice was to put the samples in the oven for 5 minutes. This is where the cliff edge is and some samples may have been on one side of the edge or the other in the past leading to inconsistent results. The chart shows the dE* for color only and color and reflectance. It is clear that the dominant change is in the reflectance of the coating.



2. The Silver 10 samples were tempered on a standard high-speed furnace and the color and sheet resistance shift were compared to the samples in the box furnace. The results matched when the samples were heated in the box furnace for 10 minutes. This was our standard for all of our tests.
3. Previously 4"x4" samples would break when removed from the box furnace. Seaming and extremely slow cool downs were needed to keep the glass from breaking. The samples heated for 10 minutes could be put in the furnace un-seamed and would not break with rapid cool down. This implies that we were not fully heating the glass at five minutes.
4. A 2"x2" samples were compared to 4"x4" for color shift with heat treatment and the results were comparable. This allowed us to HT four 2x2's at a time improving throughput by 400%.

Exhibit A

Si C-mag target

New Experiments:

These experiments started from the finishing parameters run over the weekend. Cathode 42 was run for the bottom SiN, C44 and C45 were run for the NiCr layer and C55 and C61 were run for the overcoat SiN. These conditions are the "default" conditions. All experiments vary from this initial set of conditions. Unless explicitly stated these parameters are constant for the experiments.

actual

Process Overview 2

	V tank/Vc (V)	Vo-s/Ic (mV/A)	Pc (kW)	Freq. (kHz)	Pressure (hPa)	Oxygen (sccm)	Nitrogen (sccm)	Cathode	V tank (V)	Vo-s/Ic (mV/A)	Pc (kW)	Oxygen (sccm)	Nitrogen (sccm)	Turning (sccm)
					1.66E-03			41						
SiN	191.9		11.00	24.33	2.11E-03		71.4	42	196.0		n/a		71.0	100.0
					1.96E-03			43						
NiCr	411.2	93.5	38.46		3.15E-03		35.0	44	n/a		36.75		35.0	100.0
NiCr	412.3	92.9	38.30		2.79E-03		35.1	45	n/a		36.75		35.0	100.0
					1.81E-03			51						
					6.62E-04			52						
			empty		7.79E-04	~~0~~		53						
					2.35E-03			54						
SiN	307.9		44.68	27.10	3.40E-03		270.9	55	378.0		n/a		270.0	100.0
SiN	299.0		44.72	27.21	3.98E-03		271.0	61	363.0		n/a		270.0	100.0
					1.95E-03			62						
					2.09E-03			63						
					5.08E-04			64						
					2.06E-04			65						

3.5 meter/minute linespeed

80/20 NiCr planar targets.

$mL/kw = \frac{270.9}{44.68} = 6.06$

main sputtering gas

repeat

tuning gas lag feed

tuning gas @ pump side

tuning (trim) gas @ center

tuning gas @ view side

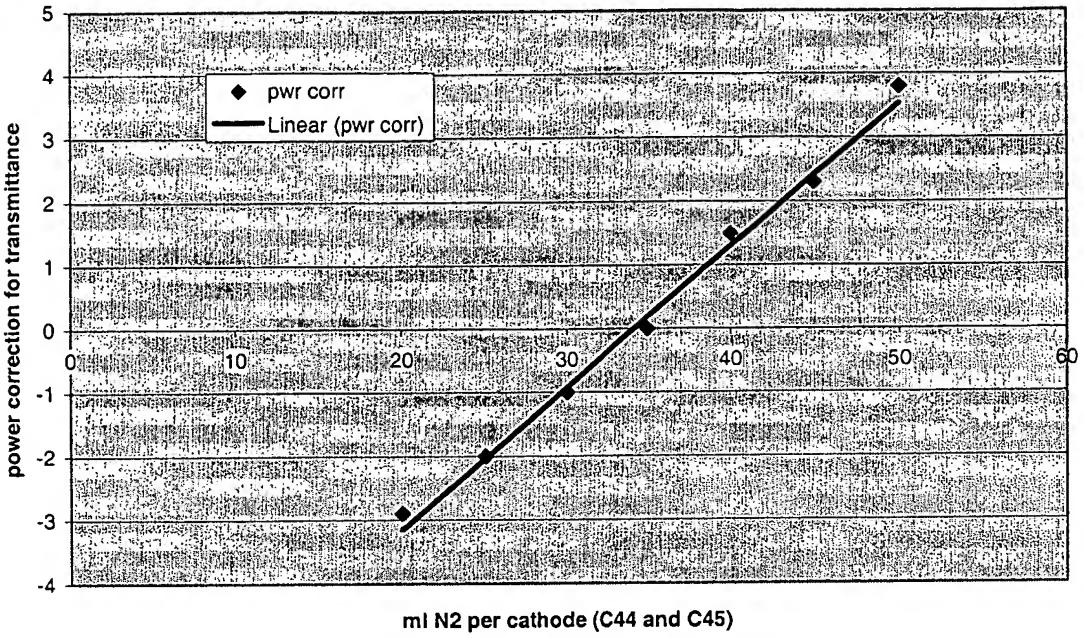
Gas Overview 2

Pressure (hPa)	Argon (sccm)	Oxygen (sccm)	Nitrogen (sccm)	Tuning Gas (sccm)	Cathode	Argon (sccm)	Oxygen (sccm)	Nitrogen (sccm)	Tunning (sccm)	Pump S. (%)	Center (%)	View S. (%)
1.66E-03	100.0	0	0		41	100.0					100.0	
2.11E-03	200.0	0	72.3	Nitrogen	42	200.0		71	100.0	45.0	5.0	50
1.96E-03	100.0	0	0		43	100.0					100.0	
3.15E-03	200.0	0	35.0	Argon	44	200.0		35	100.0	10.0	80.0	10
2.79E-03	200.0	0	35.0	Argon	45	200.0		35	100.0	20.0	70.0	10
1.81E-03	200.0	0	0	Argon	51	200.0					100.0	
6.62E-04		0	0		52						100.0	
7.79E-04		0	0		53						100.0	
2.35E-03	200.0	0	0		54	200.0					100.0	
3.40E-03	200.0		270.0	Nitrogen	55	200.0		270	100.0	45.0	5.0	50
3.98E-03	202.0		270.0	Nitrogen	61	200.0		270	100.0	45.0	5.0	50
1.95E-03	201.0				62	200.0					100.0	
2.09E-03	200.0				63	200.0					100.0	
5.08E-04	0.0		0.0	Nitrogen	64	0.0		0	0.0	0.0	0.0	0
2.06E-04	0.0		0.0	Nitrogen	65	0.0		0	0.0	0.0	0.0	0

1. The first study we conducted was a repeat of the addition of nitrogen to the NiCr cathodes. This phase repeated the trials from over the weekend to demonstrate how much nitrogen needs to be added to the process to stabilize the sheet resistance change with heat treatment and to determine what effect if any this change has on the optical color shift and physical properties of the coating.

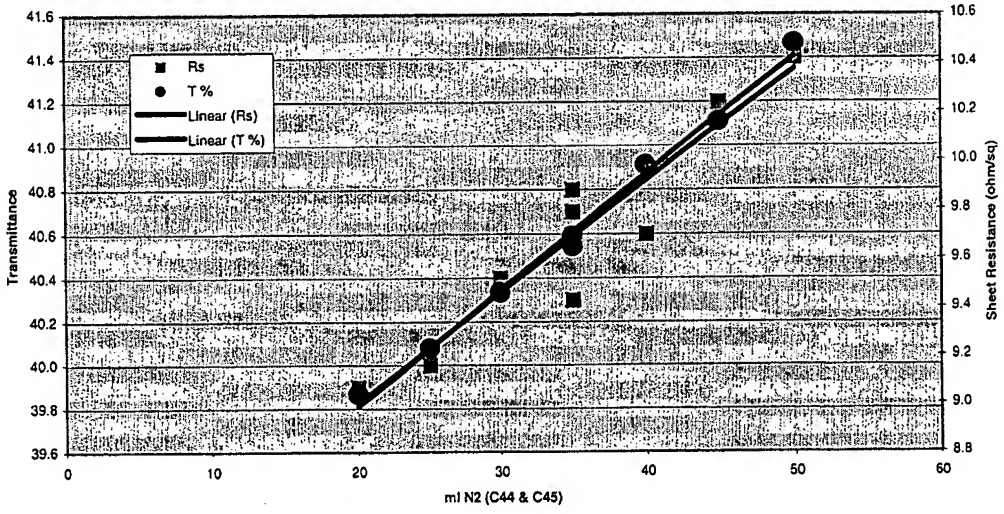
a. We ran a scan of ml of nitrogen ranging from a low of 20 to a high of 50 ml/minute. All coatings were in spec but the rate of NiCr deposition changed as a function of ml of N2 as judged by transmission. We used the color tuning chart to determine the percent increase or decrease in the NiCr thickness needed to return the transmission to the 35 ml value. We noted the new color that would accompany the change in the NiCr thickness.

Power Correction Study

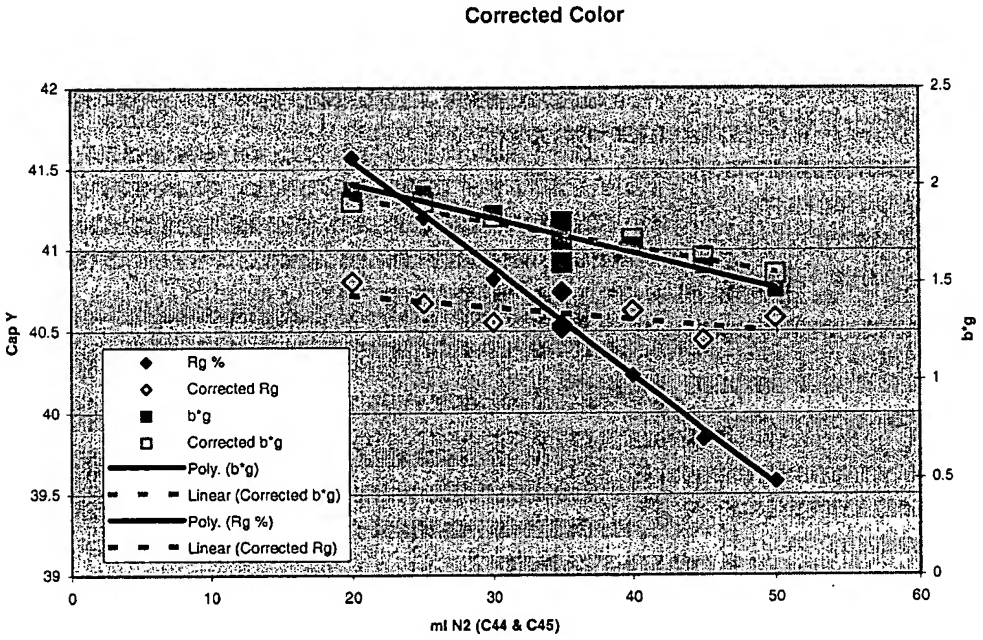


b. The effective rate varied from -2.9% for 20 ml to an increase of 3.9 for 50 ml. This is the relative change in NiCr power needed to equilibrate the transmission to the transmittance at 35 ml/minute flow of nitrogen. So... we would need to drop power for 20 ml and increase it for 50 ml. This change would account for the variation in transmittance and reflectance for this set of samples. The change in sheet resistance and transmittance with ml N2 in the NiCr cathodes is shown below.

NiCr Properties -
Transmittance and Sheet Resistance versus ml N2



c. The b*g value remained a function of ml of nitrogen even when corrected for relative thickness of NiCr. The b* was smaller at higher nitrogen flows. The only other color value that changed after thickness correction was the film side reflectance: it dropped 1% with nitrogen changes from 20 to 50 ml/minute in the NiCr cathodes. This means that there is a real change in the coating when nitrogen is present that affects the b*g value thus redefining the tuning chart for the coating.



d. The color in general would not simultaneously meet both glass side reflectance and transmittance. A move to correct one changed the other. We need to determine if this is an effect of the layer thicknesses. We built upon the last work by Leonard and Greg from the weekend but single layers were not run to compare to previous work at Carleton. The color tuning chart was used for this determination along with Excel's "Solver" function. Two examples are listed below. The first example alters the layers structures to meet the reflectance targets. The second example prioritizes the transmittance and color to the sacrifice of the glass side reflectance.

Example 1

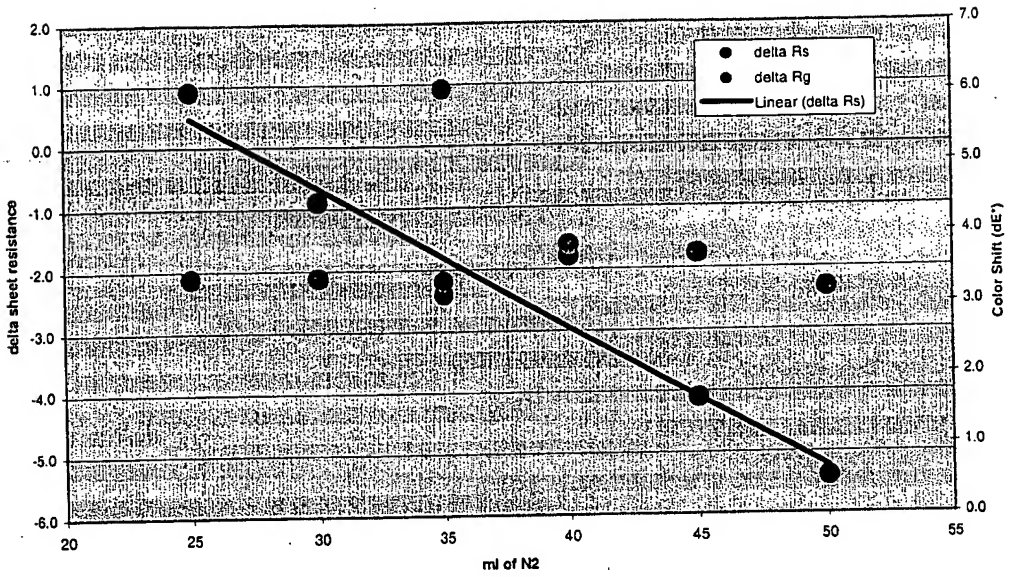
				CZ-3 Si3N4	CZ-3 Si3N4	CZ-4 NiCr	CZ-4 NiCr	CZ-5 Si3N4	CZ-5 Si3N4	Target		Optimized
Value	**Product** 130X96x6	Measured	Needed*	-10%	10%	-10%	10%	-10%	10%	Specs	Value	Specs
T %	10.0	9.7	0.3	-0.02	0.02	**2.2**	**-1.8**	-0.5	0.5	10.0	T %	8.3
Rg %	**42.0**	40.7	**1.3**	**0.11**	**-0.12**	**-2.6**	**2.1**	-0.4	0.5	42.0	Rg %	42.0
a*g	**-2.0**	-2.0	**0.0**	0.00	0.00	0.1	-0.2	-0.1	0.0	-2.0	a*g	-2.1
b*g	**2.0**	1.6	**0.4**	**-0.06**	**0.07**	-0.2	0.2	0.5	-0.6	2.0	b*g	2.0
Rf %	36.0	34.1	1.9	-0.01	0.01	**-2.1**	**1.6**	**3.4**	**-3.6**	36.0	Rf %	35.6
a*f	-0.2	0.1	-0.3	0.00	0.00	0.1	-0.1	-0.4	0.7	-0.2	a*f	0.0
b*f	22.0	22.4	-0.4	0.02	-0.02	0.3	-0.2	**-3.7**	**3.8**	22.0	b*f	22.0
Rs	**44**	40.7	**3.3**	0.0	0.0	0.5	-0.4	0.0	0.0	44.0	Rs	40.7

Example 2

				CZ-3 Si3N4	CZ-3 Si3N4	CZ-4 NiCr	CZ-4 NiCr	CZ-5 Si3N4	CZ-5 Si3N4	Target		Optimized
Value	**Product** 130X96x6	Measured	Needed*	-10%	10%	-10%	10%	-10%	10%	Specs	Value	Specs
T %	10.0	9.7	0.3	-0.02	0.02	**2.2**	**-1.8**	-0.5	0.5	10.0	T %	10.0
Rg %	**42.0**	40.7	**1.3**	**0.11**	**-0.12**	**-2.6**	**2.1**	-0.4	0.5	42.0	Rg %	39.9
a*g	**-2.0**	-2.0	**0.0**	0.00	0.00	0.1	-0.2	-0.1	0.0	-2.0	a*g	-2.0
b*g	**2.0**	1.6	**0.4**	**-0.06**	**0.07**	-0.2	0.2	0.5	-0.6	2.0	b*g	1.9
Rf %	36.0	34.1	1.9	-0.01	0.01	**-2.1**	**1.6**	**3.4**	**-3.6**	36.0	Rf %	34.2
a*f	-0.2	0.1	-0.3	0.00	0.00	0.1	-0.1	-0.4	0.7	-0.2	a*f	0.0
b*f	22.0	22.4	-0.4	0.02	-0.02	0.3	-0.2	**-3.7**	**3.8**	22.0	b*f	22.0
Rs	**44**	40.7	**3.3**	0.0	0.0	0.5	-0.4	0.0	0.0	44.0	Rs	40.7

e. The sheet resistance increased at low nitrogen and decreased at higher nitrogen relative to 35 ml N2 flow during heat treatment. The break point was between 25 and 30 ml of nitrogen.

Sheet Resistance and Color Delta's with Heat Treatment



f. The color shift was relatively constant, varying between 3.2 and 3.8 dE* except for one outlier. The majority of the color was due to a reflectance change, between 4.2 and 4.7%. This is consistent with past observations of the Silver 10 product. The a*g and b*g were virtually unchanged. This behavior was reviewed by marketing in the past and deemed acceptable. Changes to the spec to reflect this behavior will be needed. A mock-up should be scheduled at Corsicana for marketing review.

g. 35 ml flow of nitrogen was selected as our standard condition for subsequent experiments. These conditions were run periodically as a check of system reproducibility. As you can see from the table below, there is considerable "noise" in the key data. The film side dE* and dRg vary considerably. This variability must be considered when determining the effects of process parameter effects in other parts of this study.

Process Reproducibility Matrix

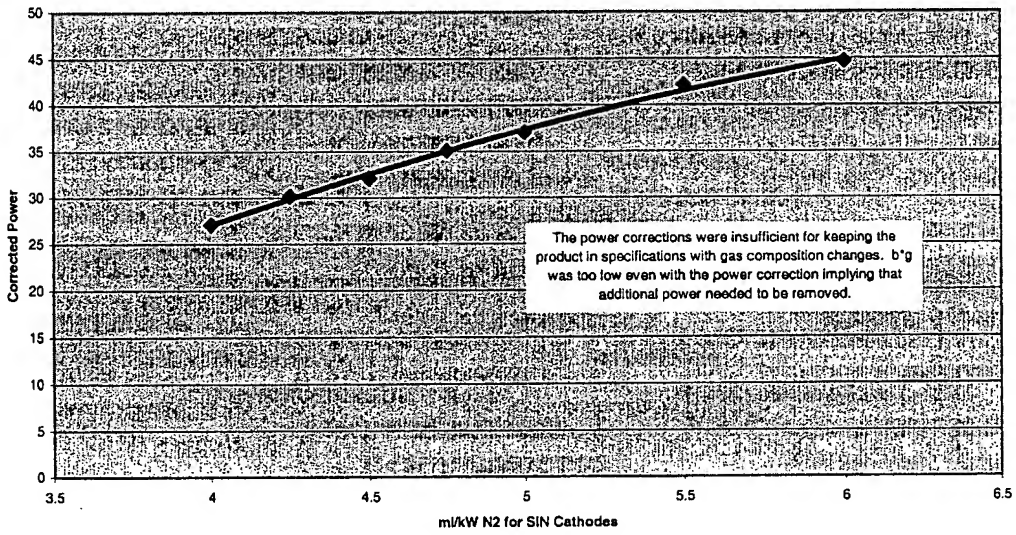
Sample ID	Annealed Taber	Sheet Annealed	Sheet HT	Sheet Delta	Rg dE*	Rg d%	Rf dE*	T dE*
9317	2.27	40.7	38.3	-2.4	6.1	-8.0	7.7	4.8
9320	2.68	40.8	38.4	-2.4	3.3	-4.4	7.0	4.9
9332	2.14	41	39.7	-1.3	4.5	-6.2	6.4	4.8
9340	2.83	42	41.4	-0.6				4.6

h. Eight samples were generated in this phase of experiments.

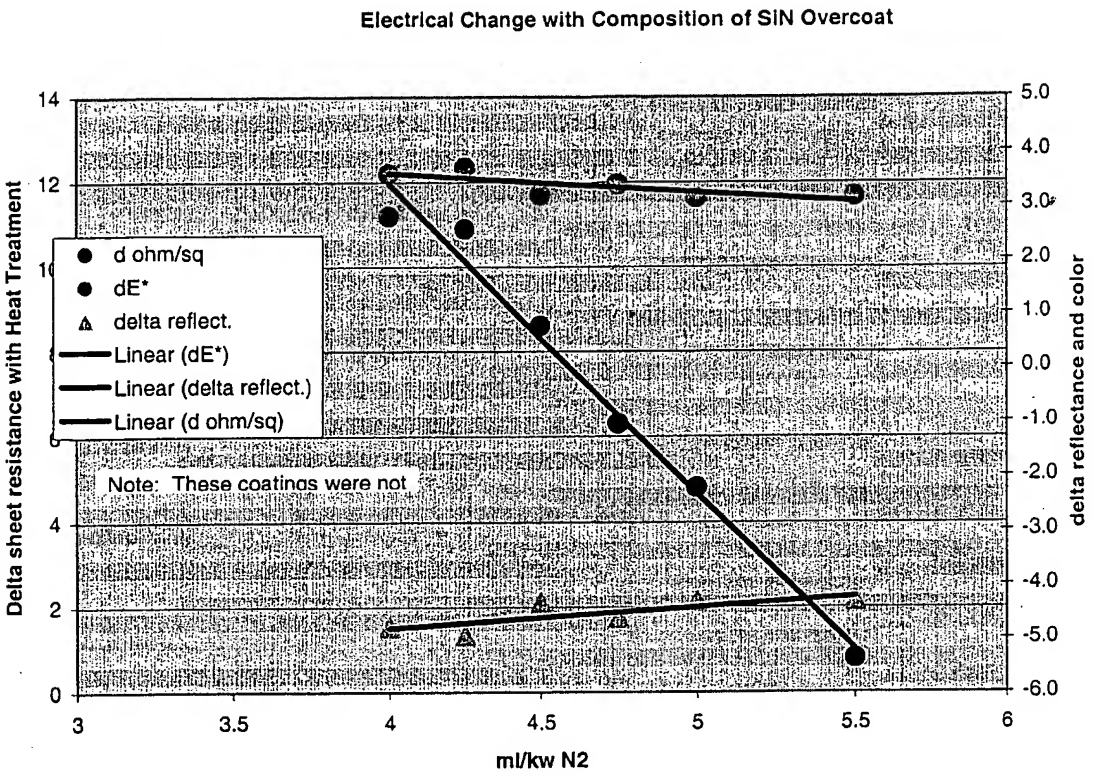
i. The samples were heat-treated and taber tested. Samples will be examined for boils pre and post bake and taber will be conducted on heat treated samples. Scratch testing will be conducted at STC. All samples will be returned to STC including large sheets.

2. The next set of experiments examined silicon nitride composition at our standard argon flow conditions. We wanted to see what effect, if any, the changing composition has on the properties of the coating with heat treatment.
    a. We have observed that the rate of deposition changes dramatically as you drop ml/kw, on the order of 10% was observed during Pewter 28 trials. We therefore adjusted power down as we dropped ml/kw so that our samples had the same overcoat thickness. Our estimates were based on Leonard's data for 150 ml argon flow. We were flowing 200 ml of Argon. We needed to drop power up to 25% more to get the coatings into spec. The thickness corrections were done in a later phase after the samples were analyzed.

Power Corrections For Deposition Rate Changes With Gas Flow



    b. The sheet resistance increased with heat treating when the ml / kw were decreased! The trend is linear. 5.5 ml/kw was relatively unchanged but the increased up to 11 ohms for 4 ml /kw. The delta E's are were between 3 and 4 units but care must be exercised as these samples are not the same design (different overcoat thicknesses). Our standard conditions are 6 ml/kw elsewhere in this study unless specifically noted.



There is an atypical behavior with the change in b* with heat treating for this set of samples. Five out of six samples have increasing b*g when traditional changes is usually decrease by about 0.50. This behavior may be the result of not having the coating centered on the color spec before heat treatment.

c. This behavior was identical to that observed during the latest Pewter 28 run. Data was distributed previously.
d. Typically the best results for taber, color shift and sheet resistance change occurred for the higher ml/kw cases.
e. Six samples were run in this phase. Testing will be the same as above.

3. The next set of experiments examined the pressure in the NiCr bays.
   a. The pressure was changed by changing the ml of argon flow in both the main gas and the tuning gas.
   b. We went from our standard 300 ml total flow to 120 ml flow in five steps.
   c. The transmittance did not change for these samples indicating that the deposition rate was constant or if it did vary then the optical constants exactly changed to match any changes with thickness due to rate changes.
   d. The color shift was constant for this set of samples
   e. The sheet resistance change varied with pressure. Lower pressure samples dropped sheet resistance more than high pressure samples.
   f. Testing will be the same as above.

4. The next set of experiments examined the effect power on the NiCr targets at constant ml of nitrogen flow.
5. The power was dropped from 38 to 12.6 kw in six equal steps. The linespeed was adjusted to keep the thicknesses constant. A constant deposition rate with power was assumed.

6. The data is not processed at this time. It has been measured for color pre and post bake. Updates will be released on Wednesday.

7. The next set of experiments examined the effect of power on the NiCr targets at constant ml/kw of nitrogen flow.
8. The power changed as above but the ml/kw were kept constant.
9. The data is not processed at this time. It has been measured for color pre and post bake. Updates will be released on Wednesday.

10. The next set of experiments examined the effect of nitrogen flow at low power.
11. The flow of nitrogen was varied with a power of 12.6 kw.
12. The flow ranged from 0 to 30 in 6 ml increments.
13. Six samples were run.
14. The data is not processed at this time. It has been measured for color pre and post bake. Updates will be released on Wednesday.

15. The next set of experiments were to correct the thicknesses of the SiN from the 200 ml argon and ml/kw study above. The NiCr nitrogen was set at 35 ml.
16. The thickness changes were estimated from the color tuning diagrams.
17. The rate at low ml/kw increased faster than predicted from the 150 ml argon flow single layer data.
18. The data is not processed at this time. It has been measured for color pre and post bake. Updates will be released on Wednesday.

19. The next set of experiments were to vary the ml/kw of nitrogen in SiN at 150 ml argon flow.
20. The samples were run in the same manner as the 200 ml argon samples but the range was expanded to 7 ml /kw due to the findings above that low ml/kw could cause increases in the sheet resistance.
21. The single layer data thicknesses were perfect predictors of how to adjust power and ml/kw simultaneously to keep thickness constant and vary composition. No corrections were needed.
22. The data is not processed at this time. It has been measured for color pre and post bake. Updates will be released on Wednesday.
23. Nine samples were run in this phase.

24. The next set of experiments was run due to the findings of lower sheet resistance changes with higher ml/kw of nitrogen flow in the SiN cathodes.
25. We wanted to repeat the ml nitrogen flow in the NiCr cathodes when the SiN's were run with 7 ml/kw flow. We ran these samples at 150 ml argon because we knew the thicknesses were constant.
26. The nitrogen flow ranged from 30 to 0 ml in 5 ml increments.
27. No changes were made to correct for changes in thickness in the NiCr.
28. The data is not processed at this time. It has been measured for color pre and post bake. Updates will be released on Wednesday.